

## Anisotropic growth of aluminum nitride nanostructures for a field emission application

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One-dimensional single-crystalline AlN nanostructures, which have a tip size of < 20 nm, were synthesized by a HVPE (halide vapor-phase epitaxy) system. The tip size and shape depend on the HCl flow rate. As the HCl flow rate increases, the tip size of the AlN nanostructure decreases. The AlN nanostructures were grown along the c-axis and preferentially oriented with their growth direction perpendicular to the substrate. The morphology and crystallinity of AlN nanorods were characterized by SEM and XRD. The chemical composition was analyzed by energy-dispersive X-ray spectroscopy in the SEM. The field emission measurements show that the turn-on field and field enhancement factor ( $\beta$ ) are 5.6 V/ $\mu\text{m}$  at a field emission current density ( $J$ ) of 10  $\mu\text{A}/\text{cm}^2$  and 2092, respectively.

**Key words:** AlN, Nanowire, Nanorod, Field emission, HVPE, CVD.

### Introduction

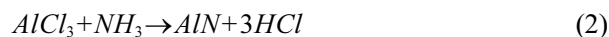
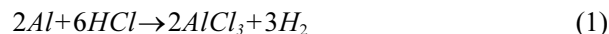
Interest in low-dimensional systems, such as zero- and one-dimensional nanostructures, has been stimulated by a desire to tune the fundamental optical and electronic properties of materials through rational control of their physical size [1, 2]. To realize the potential impact of these materials in nanoscale chemistry and physics, from both fundamental and applied viewpoints, demands materials of well-defined size, structure, and composition [1]. In the case of one-dimensional nanostructures, many studies have reported how to control of the diameter size in the liquid phase catalytic process (V-L-S growth mechanism) [1, 3, 4]. But one-dimensional nanostructures, which are grown using a non-catalytic process, have been relatively unexplored, due to the synthetic challenge of producing high-quality materials of a controlled size. The significance of the non-catalytically grown one-dimensional nanostructures originates from their sharp morphology and from well-aligned uniform arrays by which one can use them in a multitude of future electronic device applications [5].

Aluminum nitride (AlN), as well as GaN, BN, and InN, which are a group of - wide band-gap semiconductor materials, have potential applications in high-power/high-frequency electronics, acousto-optical devices, and piezoelectric devices. With a low value of electron affinity ranging from negative to nearly zero, high chemical and thermal stability, AlN should be a good candidate for field emission applications [6]. Although

some AlN nanostructures have been synthesized [7-9], there are few reports about the fabrication of size-controlled AlN nanostructure arrays and their field emission properties. In this study, we report on the size control of AlN nanorod arrays and their field emission properties.

### Experimental

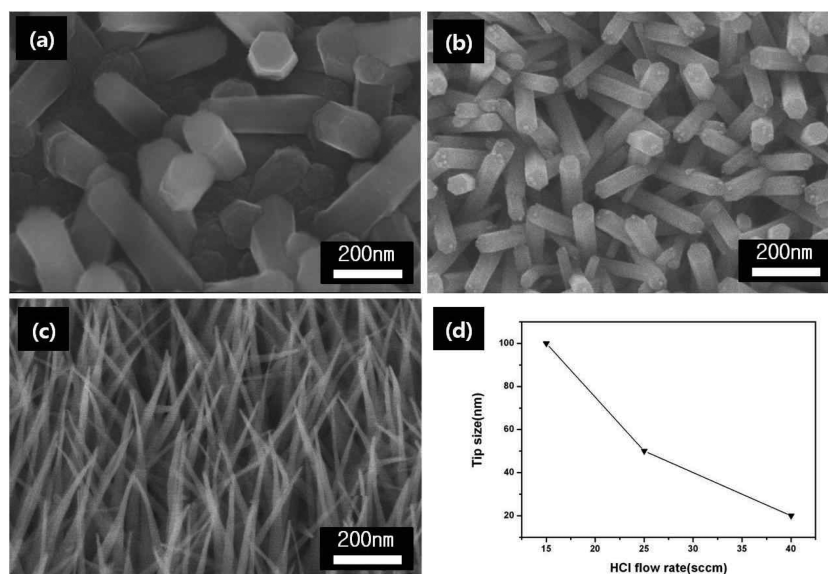
AlN nanorods were grown using the halide vapor phase epitaxy (HVPE) process on non-coated silicon substrates. The growth of AlN nanorods should follow the vapor solid (V-S) mechanism due to the absence of a liquid phase catalyst. N-type Si (100) wafers were placed in the center of a quartz tube under an ammonia atmosphere. Al metal powder and  $\text{NH}_3$  gas served as the aluminum and nitrogen sources, respectively. HCl and  $\text{N}_2$  were used as the catalyst and carrying gas. The reaction can be described as follows:



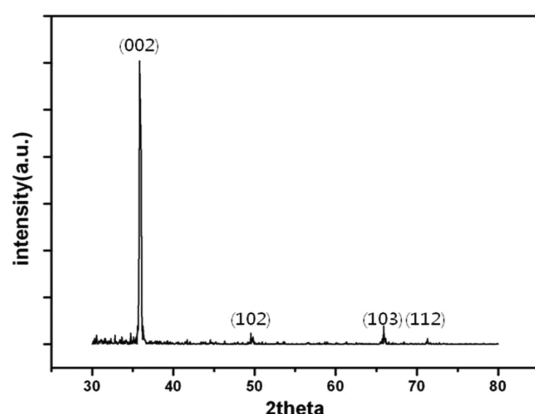
The size and shape of AlN nanorods could be controlled by the amount of HCl gas input. The HCl flow rate was in the range of 15-40 sccm and the total gas flow rate was kept at 500 sccm at 700 °C. The reaction lasted 30 minutes and the furnace was passively cooled to room temperature under a  $\text{NH}_3$  atmosphere.

The morphologies and crystalline structure of the nanorods were characterized by a scanning electron microscope (SEM) equipped with an energy-dispersive X-ray spectroscopy (EDS) detector and X-ray diffraction (XRD). The field electron emission measurements were

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**Fig. 1.** SEM images of nanorods grown with HCl flow rates of (a) 15 (sccm) (b) 25 (sccm) (c) 40 (sccm), and figure (d) Plot showing the relationship between the HCl flow rate and the tip size of nanorods.

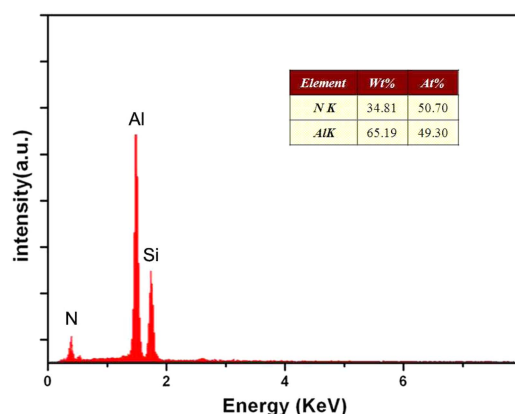


**Fig. 2.** XRD pattern of the AlN nanorod array.

performed using a parallel-plate configuration in a 7.8 MPa. Poly glass was used as spacer of 700  $\mu\text{m}$  thickness.

## Results and discussion

The size and morphology of the sample was very sensitive to the experimental parameters. In this study, the HCl flow rate acts as the most important parameter affecting the tip size and shape of the sample. Figures 1(a)–(c) show SEM images of AlN samples grown for 30 minutes on Si wafers for different HCl flow rates of 15, 25, and 40 sccm respectively. We found that the tip size of AlN nanorods was in inverse proportion to the HCl flow rate in our process (Figure 1(d)). When the HCl flow rate increases, the AlN nanorod has a smaller and sharper tip. According to this result, anisotropic growth is more energetically favorable than isotropic growth as the HCl flow rate increases. An AlN nanorod of about 20 nm diameter was synthesized under 50 sccm of HCl flow. This tip size of the AlN nanorod array in this study is smaller than that of



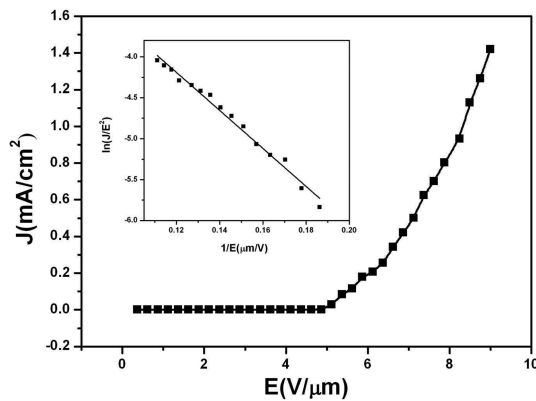
**Fig. 3.** EDS spectrum of the AlN nanorod array

previously reported AlN nanostructures [6, 11].

The XRD patterns of the nanorod were indexed to a wurtzite structure AlN (Figure 2) with lattice parameters  $a = 3.14 \text{ \AA}$  and  $c = 4.97 \text{ \AA}$ . The strong intensity of the (002) peak indicates that the AlN nanorods grew preferentially along the c-axis. Meanwhile the absence of other peaks demonstrates that no secondary phases exist.

The EDS spectrum of Figure 3 shows that the nanorods are composed of aluminum and nitrogen with an atomic ratio of 49.30 : 50.70 (approximately 1 : 1). It is quite clear that the sample is composed of only two elements (aluminum and nitrogen). The peak on the right side peak of Al indicates the silicon substrate.

The field emission measurements were performed using a parallel-plate configuration in a vacuum chamber (7.8 MPa). The silicon substrate, stainless steel, and polyglass act as cathode, anode, and spacer, respectively. Figure 4 shows the measured FE current density ( $J$ ) as a function of the applied electric field ( $E$ ) from the AlN nanorod array, which has a tip size of about 20 nm. Another sample, which had a tip size of  $> 50 \text{ nm}$  (Figure



**Fig. 4.** Field-emission current density versus electric field (J-E) for AlN nanorods. The inset shows the corresponding Fowler-Nordheim relationship.

1(a),(b)), did not emit electrons, because it had a large, flat tip. The turn-on field, defined as the electric field to obtain a current density of  $10 \mu\text{A}/\text{cm}^2$ , is  $5.6 \text{ V}/\mu\text{m}$ . According to the Fowler-Nordheim (FN) theory, the relationship between current density  $J$  and applied electric field  $E$  can be described as follows [11]:

$$J = (A\beta^2 E^2 / \phi) \exp[-B\phi^{3/2} (\beta E)^{-1}] \quad (3)$$

$$\ln\left(\frac{J}{E^2}\right) = \ln\left(\frac{A\beta^2}{\phi}\right) + \left(\frac{-B\phi^{3/2}}{\beta}\right)\left(\frac{1}{E}\right) \quad (4)$$

where  $J$  is the current density,  $E$  is the applied field,  $\Phi$  is the work function of the emitting material,  $\beta$  is the field enhancement factor, and  $A$  and  $B$  are constants with values of  $1.56 \times 10^{-10} \text{ A V}^{-2} \text{ eV}$  and  $6.83 \times 10^3 \text{ V eV}^{-3/2} \mu\text{m}^{-1}$ , respectively. The field-enhancement factor,  $\beta$ , is related to the emitter geometry, its crystal structure, and the spatial distribution of emitting centers. Because  $\beta$  can be expressed as  $\beta = h/r$ , where  $h$  is the height and  $r$  is the radius of curvature of an emitting center, materials with elongated geometry and sharp tips or edges can greatly increase an emission current [11]. The inset of Figure 4 shows the corresponding Fowler-Nordheim (FN) plots of the field emission of the AlN nanorods.

The curve shows rough linearity at high fields, indicating that the FE current originated from barrier-tunneling electrons extracted by the electric field. Based on the reported work function of AlN and the slope of the FN plot, the field enhancement factor was calculated to be  $\sim 2092$ . Compared with the previously

reported field enhancement factor of AlN nanostructures, these AlN nanorods have a larger value of  $\beta$ . With an excellent FE property, the AlN nanorods have potential applications in FE nanodevices.

## Conclusions

We have shown that AlN tip size and shape can be controlled by the HCl flow rate in the halide vapor phase epitaxy (HVPE) process. With an increase in the HCl flow rate, the tip nanorods have a sharper and smaller tip size. Nanorods, with diameters of about 20 nm, were successfully synthesized. The nanorods align uniformly along the [001] direction and were composed of aluminum and nitride with about a 1 : 1 atomic ratio. The field emission measurements show that the turn-on field is  $5.6 \text{ V}/\mu\text{m}$  at a current density of  $10 \mu\text{A}/\text{cm}^2$ , and the field enhancement factor is 2092. The nanorods have potential applications in field emission based devices.

## Acknowledgement

This research was supported by the National Space Lab (NSL) program through the National Research Foundation of Korea, funded by the Ministry of Education, Science and Technology.

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